REVIEW PAPER

Recent advances in layered $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials for lithium ion batteries

Li Wang · Jiangang Li · Xiangming He · Weihua Pu ·
Chunrong Wan · Changyin Jiang

Abstract Lithium cobalt oxide, $LiCoO_2$, has been the most widely used cathode material in commercial lithium ion batteries. Nevertheless, cobalt has economic and environmental problems that leave the door open to exploit alternative cathode materials, among which $LiNi_xCo_yMn_{1-x-y}O_2$ may have improved performances, such as thermal stability, due to the synergistic effect of the three ions. Recently, intensive effort has been directed towards the development of $LiNi_xCo_yMn_{1-x-y}O_2$ as a possible replacement for $LiCoO_2$. Recent advances in layered $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials are summarized in this paper. The preparation and the performance are reviewed, and the future promising cathode materials are also prospected.

Keywords Layered composite oxide · Cathode materials · Lithium ion battery · Review

Introduction

$LiCoO_2$ has been commercially used as a cathode material for lithium-ion batteries due to its high capacity and excellent cycling stability. Nonetheless, cobalt has economic and environmental problems that leave the door open to exploit alternative cathode materials [1–9]. For example,

L. Wang · X. He (✉) · W. Pu · C. Wan · C. Jiang
Institute of Nuclear & New Energy Technology,
Tsinghua University,
Beijing 100084, People's Republic of China
e-mail: hexm@mail.tsinghua.edu.cn

J. Li
School of Chemical Engineering,
Beijing Institute of Petrochemical Technology,
Beijing 102617, People's Republic of China

layered $LiNiO_2$ [9–12], $LiMnO_2$ [2, 13–17], and their derivatives are promising cathode materials for lithium-ion batteries due to their high theoretical capacity and low cost [18]. Unfortunately, these materials still have significant drawbacks. The major problems associated with $LiNiO_2$ include the difficulty in preparing stoichiometric $LiNiO_2$ powders without cation mixing, the structure degradation caused by irreversible phase transition during electrochemical cycling [19, 20], and thermal safety problems caused by oxygen release in the charged state. The main shortcoming of layered $LiMnO_2$ is the crystallographic transformation to spinel structure during electrochemical cycling [2, 21]. Although layered $LiMnO_2$ materials that do not convert to spinel during cycling were reported by Paulsen et al. [22], the preparation of the materials involved a cost-adding, multistep process of ion exchange of Na^+ with Li^+.

Various approaches such as partial replacement of nickel and manganese by transition metals and optimizing preparation methods and conditions were adopted to improve their performance [23–26]. For example, $LiNi_{1-x}Co_xO_2$, where $x \leq 0.4$, is considered as a promising material based on its lower price, higher specific capacity, and better cycleability. However, its thermal safety still cannot satisfy the requirements for practical applications.

The most appropriate and successful approach is to introduce Ni, Co, and Mn ions simultaneously in the layer structure [12, 27–38]. A solution of $LiNi_xCo_yMn_{1-x-y}O_2$ may possess improved performances, such as thermal stability [5, 39], due to the synergistic effect of the three ions. Therefore, recently, intensive effort has been directed towards the development of $LiNi_xCo_yMn_{1-x-y}O_2$ as a possible replacement for $LiCoO_2$ [40–46]. Dahn et al. [30, 37, 39, 47, 48] and Ohzuku et al. [29, 49, 50] did much valuable work in this field. Hwang et al. [28] reported the specific capacity of around 150–200 mAh g^{-1} for the

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ materials with a single phase and layered structure. The electrochemical performance of $LiNi_xCo_yMn_{1-x-y}O_2$ had been reported to be dependent upon structure, composition, synthesis technology, and voltage range during charge/discharge [37, 47, 51–55]. For example, $Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O_2$ with α-NaFeO$_2$ structure showed initial capacities of 165 and 195 mAh g^{-1} between 2.8–4.5 and 2.8–4.8 V, respectively, and the capacity retention decreased to 86% and 53% after 20 cycles, respectively. Yoshio et al. [56] found that the initial discharge capacity of $LiCo_{0.05}Mn_{0.2}Ni_{0.75}O_2$ is independent on the amount of the extracted Li$^+$ but kept constant between 155 and 158 mAh g^{-1}.

Structure and characterization

Similar to $LiCoO_2$, $LiNi_xCo_yMn_{1-x-y}O_2$ generally exhibits a well defined α-NaFeO$_2$ layered structure, which is hexagonal crystalline and indexed as R-3m space group [48, 57, 58]. This structure has Li$^+$ at the 3a sites, the transition metal ions M (M =Mn, Co, and Ni) at the 3b sites, and O^{2-} at the 6c sites in a MO$_6$ octahedron. X-ray diffraction is an effective methodology to investigate the crystalline structure since it gives one a good picture of the long-range structural changes in the materials [59]. The value of $I(003)/I(104)$ is used as a standard to measure the degree of the cation mixing in the layered compounds. The smaller the $I(003)/I(104)$ value, the higher the disordering. Generally, the undesirable cation mixing takes place when $I(003)/I(104)<1.2$ [27, 60]. Moreover, distinct splitting of the (108), (110), and (006), (102) peaks were also taken as the standard of a well-ordered α-NaFeO$_2$ structure [28, 61–63].

Valence analysis is very important for understanding the electrochemical mechanism of $LiNi_xCo_yMn_{1-x-y}O_2$, while it is usually complicated since the valences of Mn may be 2, 3, or 4 and Ni usually shows mixed valence [31, 49, 64, 65]. For example, Whittingham et al. [66] found that, in Li[Ni$_{0.4}$Co$_{0.2}$Mn$_{0.4}$]O$_2$ material, the valences of cobalt and 20% of the nickel are +3, while the valences of the rest of the nickel and manganese are +2 and +4 respectively. X-ray photoelectron spectroscopy [57–63], X-ray absorption near-edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) are generally the main techniques for valence analysis [28, 49, 59, 67]. Information about the valence state of the transition metal elements and their electronic configuration was generally obtained from XANES region of the K-absorption edges, whereas the EXAFS region was used to probe the structure around the X-ray absorbing atoms. In addition, XAS can distinguish between the bulk properties measurement in transmission mode and surface properties by fluorescence, or even more restricted to surface by electron yield or grazing incidence measurements. Kim et al. [68] investigated the variation of valence with charging–discharging state of the transition elements and got very important information on developing a complete understanding of the charge–discharge mechanism.

Co may stabilize the layered structure and suppress the cation mixing between 3a and 3b sites, where the Ni^{2+} and Li$^+$ cations occupy each other's sites, leading to the good performance of the materials. However, the increase of Co content results in a decrease of the lattice parameter of c and a, and an increase of the c/a ratio, leading to a decrease of the lattice cell, which decreases the capacity of the materials. Reversely, the increase of Ni content results in an increase of lattice parameter of c and a, and a decrease of the c/a ratio, leading to an increase of the lattice cell. However it benefits the capacity of the materials. However, the high content of Ni leads to the cation mixing, which deteriorates the performance of the materials. The partial substitution of Ni by Mn can improve the safety, but high content of Mn can lead to a phase transition from a layered structure to a spinel one [31]. Therefore, the contents of Ni, Co, and Mn need to be optimized for the best performance of the materials.

Cyclic voltammograms and AC impedance are helpful in understanding the electrochemical reactions and the role of every cation during charge–discharge. Generally, the redox near 3.8, 4.6, and 2.9 V can be attributed to Ni$^{2+}\rightarrow$ Ni^{4+}, Co$^{3+}\rightarrow$Co^{4+}, and Mn$^{3+}\rightarrow$Mn^{4+} [30, 69–71], respectively, while it is usually hoped that manganese is inactive to stabilize the layered structure [61].

The thermal stability of $LiNi_xCo_yMn_{1-x-y}O_2$ in electrolytes generally increases with potential decreasing. It can have remarkably higher stability than $LiCoO_2$ when the composition is adjusted. J. R. Dahn et al. [72, 73] reported that the onset temperature of $LiNi_{0.25}Co_{0.5}Mn_{0.25}O_2$ was 80 and 100 °C higher than that of $LiCoO_2$ at 4.8 and 4.2 V, respectively. Lithiated nickel oxide-based cathode materials are associated with great safety concern as they enter into an exothermic decomposition reaction with the electrolyte in the fully charged state at elevated temperatures. The exothermic reaction is attributed to the reaction of the highly oxidized Ni^{4+} ions with the organic electrolyte, which results in the evolution of flammable gases. The partial substitution of Ni by Co and Mn not only helps suppress this exothermic reaction but also shifts the reaction to a higher temperature.

Properties

The introduction of Co in the $LiNi_xCo_yMn_{1-x-y}O_2$ electrode can eliminate its cation mixing, enhance its structural stability, prevent phase transformation from layer to spinel,

and improve its electrical conductivity [57, 59, 64, 66]. Dahn et al. [72, 73] confirmed this by investigating $LiNi_{0.25}Co_{0.5}Mn_{0.25}O_2$ and $LiNi_{0.125}Co_{0.75}Mn_{0.125}O_2$. However, too much Co in the $LiNi_xCo_yMn_{1-x-y}O_2$ electrode leads to high cost and a reduction in specific capacity [71, 74]. Generally, the slightly higher content of cobalt ($0.4 \leq y \leq 0.8$) is necessary to achieve better cycle life. Consequently, it is of great importance to optimize the cobalt content in the $LiNi_xCo_yMn_{1-x-y}O_2$ material to get both applicable electrochemical performance and acceptable cost.

The increase of low-cost metals of Ni in $LiNi_xCo_y Mn_{1-x-y}O_2$ electrode could avoid electrolyte decomposition at the end of the charge potential and improve its reversible specific capacity [28, 34, 67]. However, some significant drawbacks restrict the content of Ni to a limited range. The first is cations mixing [30, 31, 64]. Since the radius of Ni^{2+} (0.069 nm) is close to that of Li^+ (0.076 nm), partial Ni^{2+} may occupy 3a sites and cause cation mixing and remarkable irreversible initial capacity. Furthermore, Ni^{3+} and Ni^{4+} produced during charging may cause the collapse of the layer structure locally, resulting in degradation of electrochemical performances [61, 75]. The partial substitution of Ni by Co can decrease the content of Ni^{2+}, leading to a decrease of the cation mixing [65].

Mn is generally electrochemically inactive in the $LiNi_xCo_yMn_{1-x-y}O_2$ electrode with good electrochemical performances, and it contributes to the safety and structural stability, and reduces the cost, of the $LiNi_xCo_yMn_{1-x-y}O_2$ electrode [59, 60]. However, superfluous Mn is the seed of phase transformation from layer to spinel [74, 76].

Kim et al. [68] investigated the roles of the transition metals in $LiNi_xCo_yMn_{1-x-y}O_2$ by neutron diffraction and situ-XAS using $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $Li_{1.1}Ni_{0.3}Co_{0.3}Mn_{0.3}O_2$, and $Li_{1.1}Ni_{0.2}Co_{0.3}Mn_{0.4}O_2$. They concluded that $LiNi_xCo_y Mn_{1-x-y}O_2$ with lower Ni/(Mn + Co) may have better stability and electrochemical performances. The degree of cation mixings has little effect on the electrochemical properties in this case. However, the Ni/(Mn + Co) ratio should be reduced to obtain good electrochemical properties with little capacity loss in this layered material. Especially after the end of the discharged state, insufficient reduction of Ni^{4+} to Ni^{2+} was observed by ex situ XAS studies, which might be one of reasons for capacity loss on the first cycle.

Lee et al. [77] found that the specific capacities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are 159, 168, and 179 mAh g^{-1} between 2.8–4.2 , 2.8–4.35 , and 2.8–4.5 V, respectively, indicating that the electrochemical performance relies on the voltage region of charge–discharge. In addition, the temperature for cycling may affect the capacity of $LiNi_x$-$Co_yMn_{1-x-y}O_2$ materials. Li et al. reported the significant effect of temperature on the electrochemical performance of $LiNi_{3/8}Co_{2/8}Mn_{3/8}O_2$ [78].

Moreover, the formation process of the cell and the electrolyte used in the cell are of great importance since they determine the interface reaction for $LiNi_xCo_yMn_{1-x-y}O_2$ electrodes. Liu et al. [79] reported that the high-rate capacity of $LiNi_xCo_yMn_{1-x-y}O_2$ electrodes changed little when formed at high rate, while it decreased markedly when formed at low rate. Besides, the effect of the formation process on $LiNi_xCo_yMn_{1-x-y}O_2$ electrodes is weaker in $LiPF_6$/EC + DMC + DEC than in Li_2BOB/EC + DEC + EMC.

Preparation and performance

The average valence of the transition metals should be + 3 to keep electron neutralization and stable structure. The popular method is to keep Ni/Mn (mol/mol) = 1:1 [60], as shown in Fig. 1, then adjust the content of Co to optimize the cost and the electrochemical performances.

The synthesis methods widely used include solid-state reaction, coprecipitation method, sol-gel method, ultrasonic spray thermal decomposition, and spray-dry method. Some typical works are shown in Table 1.

The solid-state reaction at high temperature after ball-milling is a simple process to prepare $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials. However, the particle size and morphology cannot be controlled in this method, usually leading to the poor performance of the materials. Coprecipitation, generally with carbonates, oxalates, and hydroxides, followed by high temperature calcinations, is more popular in the preparation of $LiNi_xCo_yMn_{1-x-y}O_2$ because the preparation process, as
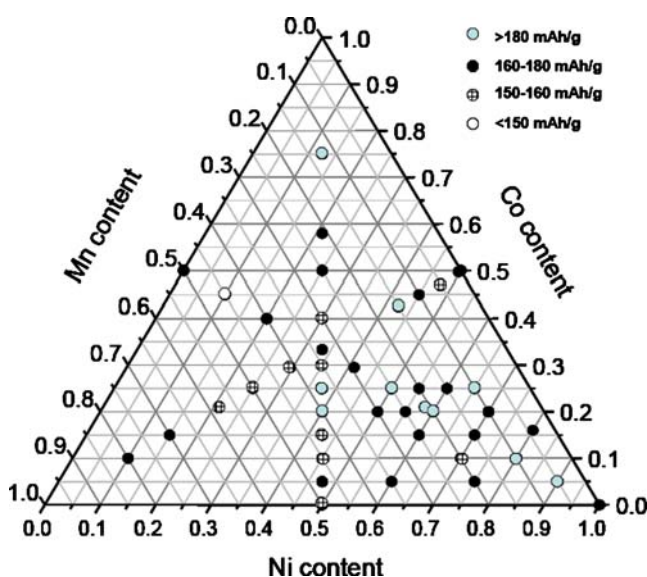

Fig. 1 The reported $LiNi_xCo_yMn_{1-x-y}O_2$

Table 1 Typical attempt on preparation of $LiNi_xCo_yMn_{1-x-y}O_2$

Researchers	Synthesis	Composition	Conclusion
Chio et al. [52]	Coprecipitation, mixed hydroxide 900 °C for 24 h	$LiNi_{0.5-y}Co_{0.5-y}Mn_{2y}O_2$ and $LiCo_{0.5-y}Mn_{0.5-y}Ni_{2y}O_2$ $LiNi_{0.5-y}Mn_{0.5-y}Co_{2y}O_2$ [81]($0\leq2x\leq1$)	Li_2MnO_3 can be observed when $2y>0.6$ in $LiNi_{0.5-y}Co_{0.5-y}M_{n2y}O_2$ and $2y<0.2$ in $LiCo_{0.5-y}Mn_{0.5-y}Ni_{2y}O_2$. The Ni-rich materials encounter a volatilization of lithium. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ is found to possess the maximal capacity and retention. The rate capability is strongly related to the cation mixing. For $LiNi_{0.5-y}Mn_{0.5-y}Co_{2y}O_2$, compositions with $0.33\leq2y\leq0.5$ exhibit high capacities (>170 mAh g^{-1} at 3.0–4.5 V and C/5 rate) and good cycleability (>90% retention in 50 cycles)
Whittingham et al. [66]	Coprecipitation mixed hydroxide	$LiCo_{0.2}Mn_{0.4}Ni_{0.4}O_2$	Discharge capacity of 180 mAh g^{-1} (2.5–4.3 V) and 155 mAh g^{-1} when the current density is 0.1 mA cm^{-2} and 2.0 mA cm^{-2}
Dahn et al. [72, 73]	Coprecipitation mixed hydroxide	$LiNi_xCo_{1-2x}Mn_xO_2$	$LiNi_{0.25}Co_{0.5}Mn_{0.25}O_2$ and $LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ exhibited good cycleability even at 4.8 V and their capacity is over 160 mAh g^{-1} between 3.0–4.2 V
Cao et al. [82]	Coprecipitation mixed hydroxide 800–900 °C in air	$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$	Initial specific discharge capacity is about 170 mAh g^{-1} (2.8–4.3 V, 0.2 C rate) and remains over 150 mAh g^{-1} and 135 mAh g^{-1} after 50 cycles and 120 cycles at 0.4 °C rate
Su et al. [83]	Coprecipitation mixed hydroxide 750 °C for 20 h	$LiNi_{0.7}Co_{0.2}Mn_{0.1}O_2$	The initial capacity is 162.99 mAh g^{-1}, and the retention is 84.17% after 10 cycles
Kan SH et al. [84]	Coprecipitation 600 °C for 16 h and then 1,000 °C for 15 h in air	$LiNi_{0.475}Mn_{0.475}Co_{0.05}O_2$	The initial capacity is over 140 mAh g^{-1} (2.8–4.3 V), and nearly no degradation within 40 cycles
Cho et al. [64]	Carbonate coprecipitation >750 °C	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	The products are spherical, and reached maximal performance when the annealing temperature is 800 °C
Ohzuku et al. [29, 49]	Coprecipitation mixed hydroxide	Li $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$	The reversible capacity after 30 is 200 mAh g^{-1} cycles (2.5–4.8 V) at 0.1 °C and 170 mAh g^{-1} at 4 °C. Similar materials prepared
Chen et al [85].	Coprecipitation mixed hydroxide	$LiCo_xMn_yNi_{1-x-y}O_2$ ($0\leq x\leq0.3$, $y=0.2$)	$LiCo_{0.1}Mn_{0.2}Ni_{0.7}O_2$ and $LiCo_{0.2}Mn_{0.2}Ni_{0.6}O_2$ showed excellent performance and their initial capacity are over 150 mAh g^{-1}
Cho TH et al. [86]	Oxalate coprecipitation 1,000 °C for 20 h in air	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	The reversible capacity is 178.6 mAh g^{-1} between 3.0–4.5 V, and the irreversible capacity loss is 12.9% at initial cycle. The rate capability was strongly influenced by particle size and specific surface area
Wang et al. [87]	Spray-drying method	$LiMn_{0.2}Co_{0.1}Ni_{0.7}O_2$, $LiMn_{0.2}Co_{0.25}Ni_{0.55}O_2$, $LiMn_{0.2}Co_{0.3}Ni_{0.5}O_2$	The initial capacity are 140–180 mAh g^{-1} and discharge voltage is lower than that of $LiCoO_2$
Oh et al. [53]	Spray-drying method	$Li[Ni_{0.5}Mn_{0.5}]_{1-x}Co_xO_2$ ($x=0.05,0.1,0.15,0.2,0.33$)	The discharge capacity increased with increasing of Co content. $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ shows capacity of over 175 mAh g^{-1} (2.8–4.4 V) as well as good cycleability
Li et al. [88]	Spray-drying method	$LiNi_{0.5-x}Mn_{0.5-x}Co_{2x}O_2$ ($0\leq x\leq0.1$)	The prepared materials all showed practicable cycleability and rate performance, among which $LiNi_{0.425}Mn_{0.425}Co_{0.15}O_2$ exhibited excellent cycleability at high temperature
Na et al. [89]	Sol-gel method in air	$LiNi_xCo_yMn_{1-x-y}O_2$	Capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is 175 mAh g^{-1} after 80 cycles
Li et al. [90]	Sol-gel method 700 °C for 7 h	$LiNi_{0.45}Co_{0.1}Mn_{0.45}O_2$	The initial capacity is about 156 mAh g^{-1} (3.0–4.3 V), and the retention is 93% after 30 cycles
Ching-Hsiang Chen et al. [61]	Sol-gel method 900 °C for 12 h	$LiNi_xCo_{1-2x}Mn_xO_2$ ($1/3\leq x\leq1/2$)	$LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ showed the best capacity of 192 mAh g^{-1}, with good cycleability at 0.1C between 3.0 and 4.5 V, which is better than $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ due to the increase of the stoichiometry of active site Ni. The performance of the $LiNi_xCo_{1-2x}Mn_xO_2$ electrode drops dramatically when $x>0.4$. The cation mixing is found if the cobalt content is less than 0.2
Son et al. [91, 92]	Sol-gel method 500 °C/ 5 h and then 1,000 °C/ 10 h in air	$Li_{1.05}Ni_{0.35}Co_{0.25}Mn_{0.4}O_2$	It has a initial discharge capacity of 164 and 187 mAh g^{-1} at 2.8–4.5 and 2.8–4.8 V respectively, applicable cycleability, and good rate capability in the current range 0.1–4.0 °C
Liao et al. [93]	Solid-state 890–950 °C in oxygen	$LiNi_{0.6}Co_{0.4-x}Mn_xO_2$ ($x=0.15,0.2,0.25$)	The capacity is 165–180 mAh g^{-1} between 3.0–4.3 V, the retention is 90% after 20 cycles. Mn is helpful to reduce the particle size
Xiao H N et al. [94]	Solid-state 800–1,050 °C for 20 h	$LiNi_{1/8}Mn_{1/8}Co_{3/4}O_2$	The initial capacity of over 217 mAh g^{-1} with coulomb efficiency of 81%, and the retention is 80% after 20 cycles
Gan et al. [95]	Solid-state 600 °C/10 h then 850 °C/10 h in air	$Li_{1.2}Ni_{0.6}Co_{0.2}Mn_{0.2}O_{2+\delta}$	The capacity declined little within 50 cycles and decline 7.2% after 100 cycles. The rate performance and thermal stability are both excellent

Table 1 (continued)

Researchers	Synthesis	Composition	Conclusion
Sun et al. [42]	Spray-pyrolysis	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	The initial capacity is 185 mAh g^{-1}, and the retention after 50 cycles is 96% at 30 °C and 94% at 55 °C, respectively
Wang X et al. [96]	Ion exchange	$Li_{2/3}(Ni_{1/3-x}Mn_{2/3-x}Co_{2x})O_2$ ($x=0.05$)	Its capacity is 188 mAh g^{-1} (2.5–4.6 V) and the coulomb efficiency was 97.5% per cycle within 30 cycles

well as the composition and morphology of the products, is easily controlled.

$LiNi_xCo_yMn_{1-x-y}O_2$ with different composition needs various synthesis conditions [77, 80]. Generally, the contents of Mn and Ni greatly influence the annealing temperature and the atmosphere, respectively. For example, $LiNi_xCo_yMn_{1-x-y}O_2$ materials with high content of Mn need high annealing temperature to get good crystal structures [12], and $LiNi_xCo_yMn_{1-x-y}O_2$ materials with high content of Ni need an oxygen atmosphere to get better layer structure. The difference among the formation conditions of Ni, Co, and Mn layered oxide leads to difficulty in preparing certain combinations in synthesis of Ni, Co, and Mn layered oxide solid solution.

Prospect

The reported $LiNi_xCo_yMn_{1-x-y}O_2$ materials have been summarized in Fig. 1. This diagram shows that $LiNi_xCo_yMn_{1-x-y}O_2$ with lower Co content ($y<0.5$) and Mn/Ni = 1:1 tends to attract more attention. Moreover, $LiNi_xCo_yMn_{1-x-y}O_2$ with Co content lower than 0.3 and Mn content lower than 0.35 were intensively investigated, and their capacities were attractive, according to the best capacity reported and summarized for every composition shown in Fig. 1. This result demonstrates that the capacity depends on the composition. For example, all the samples with capacity higher than 180 mAh g^{-1} were located on the line Co/Mn = 1:1 and Mn/Ni = 1:1, except $LiNi_{0.65}Co_{0.25}Mn_{0.1}O_2$. $LiNi_xCo_yMn_{1-x-y}O_2$ with Mn/Co = 1:1 and higher Ni content seems to have higher capacity. Besides this, the present work indicates that pure layered $LiNi_xCo_yMn_{1-x-y}O_2$ with low Ni content but Co/Mn = 1:1 and high Mn content with Co/Ni = 1:1 is hard to prepare. This figure implies that there is still much work to be done to investigate the $LiNi_xCo_yMn_{1-x-y}O_2$ cathode materials, and the high capacity and improvable cycleability make this kind of material attractive.

In addition, the capacity of $LiNi_xCo_yMn_{1-x-y}O_2$ was strongly dependent on its preparation method. For example, the capacity of $LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ prepared by solid reaction of coprecipitated triple hydroxide with LiOH at 900 °C in air for 12 h is only 154 mAh g^{-1} [58], while the capacity of $LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$ prepared by thermal decomposition of triple citric acid chelate complex at 900 °C for 12 h under oxygen flowing condition is 192 mAh g^{-1} [61]. Consequently, optimizing preparation method is a key work to produce $LiNi_xCo_yMn_{1-x-y}O_2$ with excellent performances.

Many researchers have reported the first specific discharge capacity of $LiNi_xCo_yMn_{1-x-y}O_2$ of over 180 mAh g^{-1}, as well as good cycling stability in 30 or 50 cycles when charged to 4.6 V (vs Li). However, few people have discussed the cycleability in more cycles because of the appearance of Li-branch on the surface of Li anode after many cycles.

Our lab explored the preparation of $LiNi_xCo_yMn_{1-x-y}O_2$ with the composition as shown in Fig. 2. The data labeled on the left of some compositions are their charging capacities. Compared with Fig. 1, this figure shows clearly that $LiNi_xCo_yMn_{1-x-y}O_2$ with Co/Mn=1:1 exhibits the highest capacity when x is kept constant. The capacity enhances when x increases. In addition, the efficiency for the first cycle of all the samples is 80% to 87%. It is affected by x greatly and generally increases when x decreases. Besides this, the highest data are usually possessed by samples with Co/Mn=1:1 when x is kept constant. It is worth mentioning that, though all the samples show attractive capacity, the cycleability still needs further improvements.
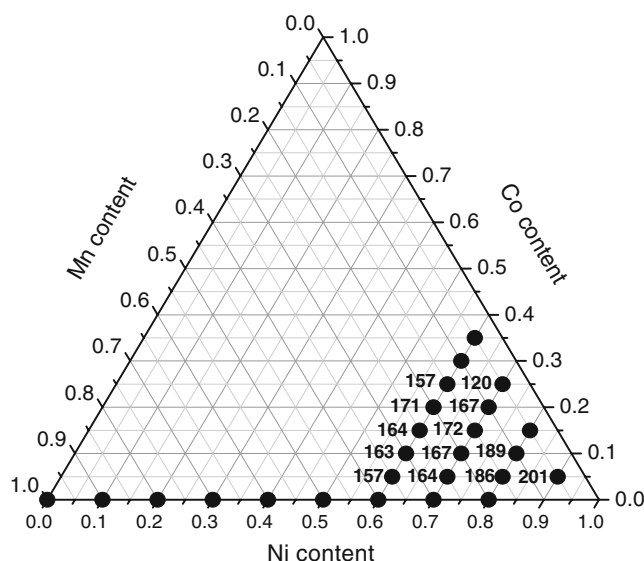

Fig. 2 $LiNi_xCo_yMn_{1-x-y}O_2$ explored by our lab

So far as we know, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ and $LiNi_{0.6-}Co_{0.2}Mn_{0.2}O_2$ are promising cathode materials for Li-ion batteries for electric vehicles since they show excellent performances, such as high capacity, good cycleability, high rate capability, high thermal stability, and high temperature performance.

Besides doping cations [97–101], substitution of O^{2-} with other anions may also improve the performance of $LiNi_xCo_yMn_{1-x-y}O_2$ [102]. The initial capacity of the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{1.96}F_{0.04}$ was 190 mAh g^{-1} and showed only 3% capacity loss after 50 cycles [103, 104]. F-substitution protected the electrode from HF attack and prevented formation of impedance-raising surface phases, so it improved the cycleability of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

In addition, coatings and composite were proven to be effective to enhance the performance of $LiNi_xCo_yMn_{1-x-y}O_2$ [66, 105, 106]. Dahn et al. found that Al_2O_3 covering improved the rate performance of $LiNi_xCo_{1-2x}Mn_xO_2$ effectively and a little B_2O_3 was helpful to enhance the tap density [107, 108]. Jang [109] improved the performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at high temperature by $Al(OH)_3$ covering. Li et al. [110] revealed that TiO_2 coating is remarkably effective at improving the cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, i.e., the capacity retention of samples at 2.5–4.3 V after 50 cycles is enhanced to 99.5% with coating amount of 2.0 mol%.

In spite of numerous valuable works, the application of $LiNi_xCo_yMn_{1-x-y}O_2$ still needs further investigations, such as to explore the synthesis method with lower temperature; to optimize the composition; and to improve the performance of $LiNi_xCo_yMn_{1-x-y}O_2$ by doping, compositing, or coating. For example, as with most potential cathode materials, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ faces problems as follows: (1) the initial irreversible capacity caused by cation mixing needs to be reduced, (2) the thermodynamic stability of the chemically delithiated materials need to be enhanced to avoid oxygen releasing and phase transformation, and (3) its discharge voltage is lower than that of $LiCoO_2$.

References

1. Armstrong AR, Bruce PG (1996) Nature 381:499 doi:10.1038/381499a0
2. Capitaine F, Gravereau P, Delmas C (1996) Solid State Ion 89:197 doi:10.1016/0167-2738(96)00369-4
3. Huang YY, Zhou HH, Chen JT (2005) Prog Inorg Chem 17:406
4. Carl JR, Bo S (2003) Sci Total Environ 302:167 doi:10.1016/S0048-9697(02)00293-0
5. Jiang J, Dahn JR (2004) Electrochem Commun 6:39–43 doi:10.1016/j.elecom.2003.10.011
6. Macneil DD, Dahn JR (2003) J Electrochem Soc 150:A21 doi:10.1149/1.1521756
7. Whittingham MS (2004) Chem Rev 104:4271 doi:10.1021/cr020731c
8. Liu YX (2005) Battery Bimon 35:196
9. Kalyani P, Kalaiselvi N (2005) Sci Technol Adv Mater 6:689 doi:10.1016/j.stam.2005.06.001
10. Delmas C, Menetrier M, Croguennec L, Saadoune I, Rougier A, Pouillerie C et al (1999) Electrochim Acta 45:243 doi:10.1016/S0013-4686(99)00208-X
11. Spahr ME, Novak P, Schnyder B (1998) J Electrochem Soc 145:1113 doi:10.1149/1.1838425
12. Hwang BJ, Tsai YW, Chen CH (2003) J Mater Chem 13:1962 doi:10.1039/b301468c
13. Armstrong AR, Bruce PG (2004) Electrochem Solid State 7:A1 doi:10.1149/1.1625591
14. Tom AE, Marca MD (2003) J Power Sources 145:119–121 doi:10.1016/S0378-7753(03)00144-7
15. Shaju KM, Sabba RGV, Chowdari BVR (2002) Electrochem Commun 4:633 doi:10.1016/S1388-2481(02)00392-2
16. Choi S, Manthiram A (2002) J Electrochem Soc 149:A1157 doi:10.1149/1.1497171
17. Guo ZP, Konstantinov K, Wang GX (2003) J Power Sources 119:221–225 doi:10.1016/S0378-7753(03)00237-4
18. Ammundsen B, Paulsen J (2001) Adv Mater 13:943 doi:10.1002/1521-4095(200107)13:12/13<943::AID-ADMA943>3.0.CO;2-J
19. Stoyanov R, Zhecheva E, Alca'ntara R (2003) Solid State Ionics 161:197 doi:10.1016/S0167-2738(03)00280-7
20. Macneil DD, Lu ZH, Dahn JR (2002) J Power Sources 108:8 doi:10.1016/S0378-7753(01)01013-8
21. Reed J, Ceder G, Van Der Ven A (2001) Electrochem Solid-State Lett 4:A78 doi:10.1149/1.1368896
22. Paulsen JM, Thomas CL, Dahn JR (1999) J Electrochem Soc 146:3560 doi:10.1149/1.1392514
23. Paulsen JM, Thomas CL, Dahn JR (2000) J Electrochem Soc 147:861 doi:10.1149/1.1393283
24. Broussely M, Perton F, Biensan P (1995) J Power Sources 54:109 doi:10.1016/0378-7753(94)02049-9
25. Rougier A, Saadoune I, Gravereau P (1996) Solid State Ion 90:83 doi:10.1016/S0167-2738(96)00370-0
26. Yamada S, Fujiwara M, Kanda M (1995) J Power Sources 54:209 doi:10.1016/0378-7753(94)02068-E
27. Liu Z, Yu A, Lee JY (1999) J Power Sources 416:81–82 doi:10.1016/S0378-7753(99)00221-9
28. Hwang BJ, Tsai YW, Carlier D (2003) Chem Mater 15:3676 doi:10.1021/cm030299v
29. Ohzuku T, Makimura Y (2001) Chem Lett 7:642 doi:10.1246/cl.2001.642
30. Lu ZH, MacNeil DD, Dahn JR (2001) Electrochem Solid-State Lett 4(12):A200 doi:10.1149/1.1413182
31. MacNeil DD, Lu Z, Dahn JR (2002) J Electrochem Soc 149:A1332 doi:10.1149/1.1505633
32. Ngala JK, Chernova NA, Ma M (2004) J Mater Chem 14:214 doi:10.1039/b309834f
33. Sun YK, Kang SH, Amine K (2004) Mater Res Bull 39:819 doi:10.1016/j.materresbull.2004.02.007
34. Lu Z, Dahn JR (2001) J Electrochem Soc 148:A237 doi:10.1149/1.1350016
35. Chen Y, Wang GX, Konstantinov K (2003) J Power Sources 184:119–2121
36. Ryuji S, Akihiro F, Kazuya O (2004) EP: 1447866A1

37. Jouanneau S, Eberman KW, Krause LJ (2003) J Electrochem Soc 150:A1637 doi:10.1149/1.1622956
38. Jin SJ, Park KS, Song CH (2005) J Power Sources 146:630 doi:10.1016/j.jpowsour.2005.03.167
39. Jouanneau S, Macneil DD, Dahn JR (2003) J Electrochem Soc 150:A1299 doi:10.1149/1.1602077
40. Lee MH, Kang YJ, Myung ST (2004) Electrochim Acta 50:939 doi:10.1016/j.electacta.2004.07.038
41. Kalyani P, Kalaiselvi N, Renganathan NG (2004) Mater Res Bull 39:41 doi:10.1016/j.materresbull.2003.09.021
42. Park SH, Yoon CS, Kang G (2004) Electrochim Acta 49:557 doi:10.1016/j.electacta.2003.09.009
43. Albrecht S, Kümpers J, Kruft M (2003) J Power Sources 178:119–121 doi:10.1016/S0378-7753(03)00175-7
44. Vasanthi R, Ruth MI, Selladurai S (2003) Inorg Chem Commun 6:953 doi:10.1016/S1387-7003(03)00159-X
45. Hironori K, Yoshinori A, Hiroyuki K (2004) J Mater Chem 14:40 doi:10.1039/b311827d
46. Gopukumar S, Chung KY, Kim KB (2004) Electrochim Acta 49:803 doi:10.1016/j.electacta.2003.09.034
47. Jouanneau S, Dahn JR (2003) Chem Mater 15:495 doi:10.1021/cm020818e
48. Paulsen JM, Mueller-Neuhaus JR, Dahn JR (2000) J Electrochem Soc 147:508 doi:10.1149/1.1393225
49. Koyama Y, Tanaka I, Ohzuku T (2003) J Power Sources 644:119–121 doi:10.1016/S0378-7753(03)00194-0
50. Yabuuchi N, Ohzuku T (2003) J Power Sources 171:119–121 doi:10.1016/S0378-7753(03)00173-3
51. Li JG, He XM, Zhao RS (2006) J Power Sources 158:524 doi:10.1016/j.jpowsour.2005.08.026
52. Choi J, Manthiram A (2006) J Power Sources 162:667 doi:10.1016/j.jpowsour.2006.06.031
53. Oh SW, Park SH, Park CW (2004) Solid State Ion 171:167 doi:10.1016/j.ssi.2004.04.012
54. Arunkumar TA, Alvarez E, Manthiram A (2007) J Electrochem Soc 154:A770 doi:10.1149/1.2745635
55. Tran N, Croguennec L, Jordy C (2005) Solid State Ion 176:1539 doi:10.1016/j.ssi.2005.04.039
56. Yoshio M, Noguchi H, Itoh J (2000) J Power Sources 90:176 doi:10.1016/S0378-7753(00)00407-9
57. Shaju KM, Subba Rao GV, Chowdari BVR (2002) Electrochim Acta 48:145 doi:10.1016/S0013-4686(02)00593-5
58. Sun YC, Ouyang CY, Wang ZX (2004) J Electrochem Soc 151:A504 doi:10.1149/1.1647574
59. Deb A, Bergmann U, Cramer SP, Cairnsa EJ (2007) J Electrochem Soc 154:A534 doi:10.1149/1.2720762
60. Gao Y, Yakovleva M, Wang HH (2003) US-6–620–400
61. Chen CH, Wang CJ, Hwang BJ (2005) J Power Sources 146:626 doi:10.1016/j.jpowsour.2005.03.079
62. Ohzuku T, Makimura Y (2001) Chem Lett 7:642 doi:10.1246/cl.2001.642
63. Gao YA, Yakovleva MV, Ebner WB (1998) Electrochem Solid-State Lett 1:117 doi:10.1149/1.1390656
64. Cho YH, Park SM, Yoshio M (2005) J Power Sources 142:306 doi:10.1016/j.jpowsour.2004.10.016
65. Lu ZH, Macneil DD, Dahn JR (2001) Electrochem Solid-State Lett 4:A191 doi:10.1149/1.1407994
66. Ngala JK, Chernova NA, Whittingham MS (2004) J Mater Chem 14:214 doi:10.1039/b309834f
67. Deb A, Bergmann U, Cramer SP (2005) J Appl Phys 97:113523 doi:10.1063/1.1921328
68. Kim JM, Hoon-Taek C (2004) Electrochim Acta 49:3573 doi:10.1016/j.electacta.2004.03.025
69. Paulsen M, Thomas CL, Dahn JR (2000) J Electrochem Soc 147:861 doi:10.1149/1.1393283
70. Kim JH, Park CW, Sun YK (2003) Solid State Ion 164:43 doi:10.1016/j.ssi.2003.08.003
71. Kim JS, Johnson CS, Thackeray MM (2002) Electrochem Commun 4:205 doi:10.1016/S1388-2481(02)00251-5
72. Jouanneau S, Macneil DD, Dahn JR (2003) J Electrochem Soc 150:A1299 doi:10.1149/1.1602077
73. Jouanneau S, Eberman KW, Dahn JR (2003) J Electrochem Soc 150:A1637 doi:10.1149/1.1622956
74. Masaki Y, Hideyuki N, Okada TM (2000) J Power Sources 90:176 doi:10.1016/S0378-7753(00)00407-9
75. Saadoune I, Delmas C (1998) J Solid State Chem 136:8 doi:10.1006/jssc.1997.7599
76. Venkatraman S, Choi J, Manthiram A (2004) Electrochem Commun 6:832 doi:10.1016/j.elecom.2004.06.004
77. He P, Wang HR, Qia L (2006) J Power Sources 160:627 doi:10.1016/j.jpowsour.2006.01.053
78. Li JG, Wan CR, Yang DP (2003) Acta Phys-Chim Sin 19:1030
79. Liu JJ, Qiu WH, Yu LY (2006) Electrochem 12:373
80. Luo XF, Wang XY, Liao L (2006) J Power Sources 161:601 doi:10.1016/j.jpowsour.2006.03.090
81. Choi J, Manthiram A (2005) Solid State Ion 176:2251 doi:10.1016/j.ssi.2005.06.004
82. Cao H, Zhang Y, Zhang J (2005) Solid State Ion 176:1207 doi:10.1016/j.ssi.2005.02.023
83. Su YC, Xie W, Yu P (2005) Mater Sci Eng Powder Metall 10:149
84. Kang SH, Kim J, Stoll ME (2002) J Power Sources 112:41 doi:10.1016/S0378-7753(02)00360-9
85. Chen Y, Wang GX, Konstantinov K (2003) J Power Sources 184:119–121 doi:10.1016/S0378-7753(03)00176-9
86. Cho TH, Shiosaki Y, Noguchi H (2006) J Power Sources 159:1322 doi:10.1016/j.jpowsour.2005.11.080
87. Wang GX, Bewlay S, Yao J (2003) J Power Sources 189:119–121 doi:10.1016/S0378-7753(03)00177-0
88. Li DC, Noguchi H, Yoshio M (2004) Electrochim Acta 50:427 doi:10.1016/j.electacta.2004.04.045
89. Na SH, Kim HS, Moon SI (2005) Solid State Ion 176:313 doi:10.1016/j.ssi.2004.08.016
90. Li P, Han ES, Tan BS (2005) Chin J Appl Chem 22:304
91. Son JT, Cairns EJ (2006) Electrochem Solid-State Lett 9:A27 doi:10.1149/1.2136248
92. Son JT, Cairns EJ (2007) J Power Sources 166:343 doi:10.1016/j.jpowsour.2006.12.069
93. Liao PY, Duh JG, Sheen SR (2005) J Power Sources 143:212 doi:10.1016/j.jpowsour.2004.12.001
94. Xiao HN, Yi WW, Hu PF (2006) China ceram Ind 13:1
95. Gan CL, Hu XH, Zhan H (2005) Solid State Ion 176:687 doi:10.1016/j.ssi.2004.10.021
96. Wang X, Yang XH, Zheng HG (2005) Solid State Ion 176:1043 doi:10.1016/j.ssi.2005.01.003
97. Park SH, Oh SW, Sun YK (2005) J Power Sources 146:622 doi:10.1016/j.jpowsour.2005.03.078
98. Kim GH, Myung ST, Bang HJ (2004) Electrochem Solid-State Lett 7:A477 doi:10.1149/1.1809554
99. Meng YS, Wu YW, Hwang BJ (2004) J Electrochem Soc 151:A1134 doi:10.1149/1.1765032
100. Li DC, Sasaki Y, Kobayakawa K (2006) J Power Sources 157:488 doi:10.1016/j.jpowsour.2005.08.023
101. Li JG, He XM, Zhao RS (2006) J Power Sources 158:524 doi:10.1016/j.jpowsour.2005.08.026
102. Kang SH, Amine K (2005) J Power Sources 146:654 doi:10.1016/j.jpowsour.2005.03.152
103. Kim GH, Kim JH, Myung ST (2005) J Electrochem Soc 152:A1707 doi:10.1149/1.1952747
104. Woo SU, Park BC, Yoon CS (2007) J Electrochem Soc 154:A649 doi:10.1149/1.2735916

105. Cho J, Kim YW, Kim B (2003) Angew Chem Int Ed 42:1618 doi:10.1002/anie.200250452

106. Kim HS, Kong M, Kim K (2007) J Power Sources 171:917 doi:10.1016/j.jpowsour.2007.06.028

107. Jouanneau S, Bahmet W, Eberman KW (2004) J Electrochem Soc 151:A1789 doi:10.1149/1.1799411

108. Kim Y, Kim HS, Martin SW (2006) Electrochim Acta 52:1316 doi:10.1016/j.electacta.2006.07.033

109. Jiang SB, Kang SH, Amine K (2005) Electrochim Acta 50:4168 doi:10.1016/j.electacta.2005.01.037

110. Li JG, Fan MS, He XM (2006) Ionics 12:215 doi:10.1007/s11581-006-0034-2